



Boyer, H., Bzdek, B., Reid, J., & Dutcher, C. (2017). A Statistical Thermodynamic Model for Surface Tension of Organic and Inorganic Aqueous Mixtures. *Journal of Physical Chemistry A*, 121(1), 198-205. <https://doi.org/10.1021/acs.jpca.6b10057>

Peer reviewed version

Link to published version (if available):  
[10.1021/acs.jpca.6b10057](https://doi.org/10.1021/acs.jpca.6b10057)

[Link to publication record on the Bristol Research Portal](#)  
PDF-document

This is the author accepted manuscript (AAM). The final published version (version of record) is available online via ACS at <http://pubs.acs.org/doi/abs/10.1021/acs.jpca.6b10057>. Please refer to any applicable terms of use of the publisher.

## University of Bristol – Bristol Research Portal

### General rights

This document is made available in accordance with publisher policies. Please cite only the published version using the reference above. Full terms of use are available: <http://www.bristol.ac.uk/red/research-policy/pure/user-guides/brp-terms/>

# Supporting Information for “A Statistical Thermodynamic Model for Surface Tension of Organic and Inorganic Aqueous Mixtures”

Hallie C. Boyer<sup>a</sup>, Bryan R. Bzdek<sup>b</sup>, Jonathan P. Reid<sup>b</sup> and Cari S. Dutcher<sup>a\*</sup>

(cdutcher@umn.edu)

<sup>a</sup>Department of Mechanical Engineering, University of Minnesota, Twin Cities, Minneapolis, MN 55455, USA.

<sup>b</sup>School of Chemistry, University of Bristol, BS8 1TS, UK.

## Statistical Mechanical Derivation for an Arbitrary Number of Solutes

For an arbitrary number of solutes,  $n$ , we define the number of possible configurations of at the surface in eq S1, the surface partition function. Subscript  $j$  of the first multiplicative sum represents the solute that adsorbs at the surface (or bulk) first, where each solute in the system from A to Z has this position  $(n-1)!$  times. Solute  $k$  of the next multiplicative sum represents all solutes except for  $j$ , with the notation  $k < j$  meaning the subsequent solutes that have the second spot in line  $(n-2)!$  times. The multiplicative sums are defined as needed for however many solutes are in the system. With this approach, there is a unique combination for each permutation of solute adsorption, making a total of  $n!$  possible surface partition functions. Therefore, the entire product is raised to the power  $1/n!$ , resulting in

$$\Omega_{surface} = \left\{ \prod_j^Z \prod_{k < j} \prod_{l < k} \dots \frac{N_{WS}! r_j^{(n-1)!} (N_{WS} - r_k N_{kS})! r_j^{(n-2)!} (N_{WS} - r_k N_{kS} - r_l N_{lS})! r_j^{(n-3)!} \dots}{(r_j N_{jS})! r_j^{n!} (N_{WS} - r_j N_{jS})! r_j^{(n-1)!} (N_{WS} - r_j N_{jS} - r_k N_{kS})! r_k^{(n-2)!} (N_{WS} - r_j N_{jS} - r_k N_{kS} - r_l N_{lS})! r_l^{(n-3)!} \dots} \right\}^{1/n!} \quad (S1)$$

The bulk partition function represents mixing between the surface and the bulk for each solute:

$$\Omega_{bulk} = \prod_{j=A}^Z \frac{N_j!}{N_{jS}! (N_j - N_{jS})!} \quad (S2)$$

Gibbs free energy,  $G \approx E - TS$ , must be found next. We obtain an expression for entropy through Boltzmann's equation,  $S = k_B \text{Ln} \Omega_{bulk} \Omega_{surface}$ , giving

$$\begin{aligned} & \frac{S}{k_B} \\ &= \frac{1}{n!} \left\{ \sum_{j=A}^Z N_j \text{Ln} \left( \frac{N_j}{N_j - N_{jS}} \right) \right. \\ &+ \sum_{k < j} \sum_{l < k} \dots \frac{N_{WS}}{r_j} \text{Ln} \left( \left( \frac{N_{WS}}{N_{WS} - r_j N_{jS}} \right)^{(n-1)!} \left( \frac{r_k (N_{WS} - r_k N_{kS})}{r_j (N_{WS} - r_j N_{jS} - r_k N_{kS})} \right)^{(n-2)!} \right. \\ &\quad \left. \left( \frac{r_l (N_{WS} - r_k N_{kS} - r_l N_{lS})}{r_j (N_{WS} - r_j N_{jS} - r_k N_{kS} - r_l N_{lS})} \right)^{(n-3)!} \dots \right) \\ &+ N_{jS} \text{Ln} \left( \left( \frac{N_j - N_{jS}}{N_{jS}^2} \right)^{n!} \left( \frac{N_{WS} - r_j N_{jS}}{r_j} \right)^{(n-1)!} \left( \frac{N_{WS} - r_j N_{jS} - r_k N_{kS}}{r_k} \right)^{(n-2)! r_j / r_k} \right. \\ &\quad \left. \left( \frac{N_{WS} - r_j N_{jS} - r_k N_{kS} - r_l N_{lS}}{r_l} \right)^{(n-3)! r_j / r_l} \dots \right) \\ &+ N_{kS} \text{Ln} \left( \left( \frac{N_{WS} - r_j N_{jS} - r_k N_{kS}}{r_k} \right)^{(n-2)!} \left( \frac{r_j}{(N_{WS} - r_k N_{kS})} \right)^{(n-2)! r_k / r_j} \right. \\ &\quad \left. \left( \frac{N_{WS} - r_j N_{jS} - r_k N_{kS} - r_l N_{lS}}{r_l} \right)^{(n-3)! r_k / r_l} \left( \frac{r_j}{(N_{WS} - r_k N_{kS} - r_l N_{lS})} \right)^{(n-3)! r_k / r_j} \dots \right) \\ &+ N_{lS} \text{Ln} \left( \left( \frac{N_{WS} - r_j N_{jS} - r_k N_{kS} - r_l N_{lS}}{r_l} \right)^{(n-3)!} \left( \frac{r_j}{(N_{WS} - r_k N_{kS} - r_l N_{lS})} \right)^{(n-3)! r_l / r_j} \dots \right) \dots \left. \right\}. \end{aligned} \quad (S3)$$

The total energy is the sum of molecular energies of waters at the surface ( $\epsilon_{WS}$ ), waters in the bulk ( $\epsilon_{WB}$ ), solutes at the surface ( $\epsilon_{jS}$ ) and solutes in the bulk ( $\epsilon_{jB}$ ) multiplied by the number of each, giving

$$E = -N_{WS}\Delta\epsilon_{WS} - N_W\epsilon_{WB} - \sum_{j=A}^Z (N_{jS}\Delta\epsilon_{jS} - N_j\epsilon_{jB}) \quad (\text{S4})$$

Solute activity is the derivative of  $G$  with respect to number of solutes in the system,  $N_j$ , resulting in

$$K_j a_j = 1 - \frac{N_{jS}}{N_j} \quad (\text{S5})$$

where  $K_j = \exp\left(\frac{\Delta\epsilon_{jB}}{k_B T}\right)$ . Equilibrium partitioning of a solute between the surface and bulk is imposed by taking the derivative of  $G$  with respect to number of solutes at the surface,  $N_{jS}$ , and setting it equal to zero, resulting in

$$\begin{aligned} C_j &= \exp\left(\frac{\Delta\epsilon_{jS}}{k_B T}\right) \\ &= \prod_{k<j} \prod_{l<k} \dots \frac{N_{jS}^2}{N_j - N_{jS}} \left\{ \left( \frac{r_j}{N_{WS} - r_j N_{jS}} \right)^{(n-1)!} \left( \frac{r_j}{N_{WS} - r_j N_{jS} - r_k N_{kS}} \right)^{(n-2)!} \right. \\ &\quad \times \left( \frac{r_j}{N_{WS} - r_j N_{jS} - r_k N_{kS} - r_l N_{lS}} \right)^{(n-3)!} \\ &\quad \times \left( \frac{N_{WS} - r_j N_{jS}}{N_{WS} - r_j N_{jS} - r_k N_{kS}} \right)^{(n-2)! r_j / r_k} \\ &\quad \times \left( \frac{N_{WS} - r_j N_{jS} - r_k N_{kS}}{N_{WS} - r_j N_{jS} - r_k N_{kS} - r_l N_{lS}} \right)^{(n-3)! r_j / r_l} \\ &\quad \times \left( \frac{N_{WS} - r_j N_{jS} - r_k N_{kS}}{r_k} \right)^{(n-3)! r_j / r_l} \\ &\quad \left. \times \left( \frac{r_l}{N_{WS} - r_j N_{jS} - r_k N_{kS} - r_l N_{lS}} \right)^{(n-3)! r_j / r_l} \right\} \frac{1}{n!} \end{aligned} \quad (\text{S6})$$

Surface tension is obtained by taking the derivative of  $G$  with respect to area, approximated as the projected area of one water molecule,  $S_W$ , times the maximum number of waters at the surface,

$N_{WS}$ . There are also solutes at the surface, so area occupied by solutes is actually  $r_j N_{jS} S_W$  and the area occupied by waters is  $S_W(N_{WS} - r_j N_{jS})$ , making the total area  $S_W N_{WS}$ . The expression for surface tension is

$$\begin{aligned} \sigma &= \sigma_w \\ &+ \sum_{j=A}^Z \sum_{k < j} \sum_{l < k} \dots \frac{kT}{r_j S_W} \frac{1}{n!} \text{Ln} \left( \left( \frac{N_{WS} - r_j N_{jS}}{N_{WS}} \right)^{(n-1)!} \left( \frac{r_j (N_{WS} - r_j N_{jS} - r_k N_{kS})}{r_k (N_{WS} - r_k N_{kS})} \right)^{(n-2)!} \right. \\ &\quad \left. \left( \frac{r_j (N_{WS} - r_j N_{jS} - r_k N_{kS} - r_l N_{lS})}{r_l (N_{WS} - r_k N_{kS} - r_l N_{lS})} \right)^{(n-3)!} \dots \right) \end{aligned} \quad (\text{S7})$$

Equations S3, S6, and S7 are evaluated for 1, 2, and 3 solute systems in the Supporting Information in Tables S1-S3. Let  $\chi_{AB} = N_{WS} - r_A N_{AS} - r_B N_{BS}$ ,  $\chi_{AC} = N_{WS} - r_A N_{AS} - r_C N_{CS}$ ,  $\chi_{ABC} = N_{WS} - r_A N_{AS} - r_B N_{BS} - r_C N_{CS}$ , and so forth.

**Table S1:** Equation 3 evaluated for solutions containing one, two, and three solutes.

Number of solutes ( $n$ )	Entropy ( $S/k_B$ )
$n=1$	$N_A \ln \left( \frac{N_A}{N_A - N_{AS}} \right) + \frac{N_{WS}}{r_A} \left( \frac{N_{WS}}{N_{WS} - r_A N_{AS}} \right) + \frac{(N_{WS} - r_A N_{AS})(N_A - N_{AS})}{r_A N_{AS}^2}$
$n=2$	$N_A \ln \frac{N_A}{(N_A - N_{AS})} + N_B \ln \frac{N_B}{(N_B - N_{BS})} + \frac{N_{WS}}{2r_A} \ln \frac{N_{WS}(N_{WS} - r_B N_{BS})}{\chi_{AB}(N_{WS} - r_A N_{AS})}$ $+ \frac{N_{WS}}{2r_B} \ln \frac{N_{WS}(N_{WS} - r_A N_{AS})}{\chi_{AB}(N_{WS} - r_B N_{BS})} + \frac{r_A N_{AS}}{2r_B} \ln \frac{\chi_{AB}}{(N_{WS} - r_A N_{AS})}$ $+ \frac{r_B N_{BS}}{2r_A} \ln \frac{\chi_{AB}}{(N_{WS} - r_B N_{BS})}$ $+ \frac{N_{AS}}{2} \ln \frac{\chi_{AB}(N_{WS} - r_A N_{AS})(N_A - N_{AS})^2}{r_A^2 N_{AS}^4}$ $+ \frac{N_{BS}}{2} \ln \frac{\chi_{AB}(N_{WS} - r_B N_{BS})(N_B - N_{BS})^2}{r_B^2 N_{BS}^2}$

$n=3$	$ \begin{aligned} & N_A \text{Ln} \frac{N_A}{(N_A - N_{AS})} + N_B \text{Ln} \frac{N_B}{(N_B - N_{BS})} + N_C \text{Ln} \frac{N_C}{(N_C - N_{CS})} \\ & + \frac{N_{AS}}{6} \text{Ln} \left[ \frac{(N_A - N_{AS})^6 \chi_{AB} \chi_{AC} \chi_A^2 \chi_{ABC}^2}{r_A N_{AS}^{12}} \right] \\ & + \frac{N_{BS}}{6} \text{Ln} \left[ \frac{(N_B - N_{BS})^6 \chi_{AB} \chi_{BC} \chi_B^2 \chi_{ABC}^2}{r_B N_{BS}^{12}} \right] \\ & + \frac{N_{CS}}{6} \text{Ln} \left[ \frac{(N_C - N_{CS})^6 \chi_{AC} \chi_{BC} \chi_C^2 \chi_{ABC}^2}{r_C N_{CS}^{12}} \right] \\ & + \frac{N_{WS}}{6r_A} \text{Ln} \frac{N_{WS}^2 \chi_B \chi_C \chi_{BC}^2}{\chi_{AC} \chi_{AB} \chi_A^2 \chi_{ABC}^2} + \frac{N_{WS}}{6r_B} \text{Ln} \frac{N_{WS}^2 \chi_A \chi_C \chi_{AC}^2}{\chi_{BC} \chi_{AB} \chi_B^2 \chi_{ABC}^2} \\ & + \frac{N_{WS}}{6r_C} \text{Ln} \frac{N_{WS}^2 \chi_A \chi_B \chi_{AB}^2}{\chi_{AC} \chi_{BC} \chi_C^2 \chi_{ABC}^2} + \frac{r_A N_{AS}}{6r_B} \text{Ln} \frac{\chi_{AB} \chi_{ABC}^2}{\chi_A \chi_{AC}^2} \\ & + \frac{r_A N_{AS}}{6r_C} \text{Ln} \frac{\chi_{AC} \chi_{ABC}^2}{\chi_A \chi_{AB}^2} + \frac{r_B N_{BS}}{6r_C} \text{Ln} \frac{\chi_{BC} \chi_{ABC}^2}{\chi_B \chi_{AB}^2} + \frac{r_B N_{BS}}{6r_A} \text{Ln} \frac{\chi_{AB} \chi_{ABC}^2}{\chi_B \chi_{BC}^2} \\ & + \frac{r_C N_{CS}}{6r_B} \text{Ln} \frac{\chi_{BC} \chi_{ABC}^2}{\chi_C \chi_{AC}^2} + \frac{r_C N_{CS}}{6r_A} \text{Ln} \frac{\chi_{AC} \chi_{ABC}^2}{\chi_C \chi_{BC}^2} \end{aligned} $
-------	---

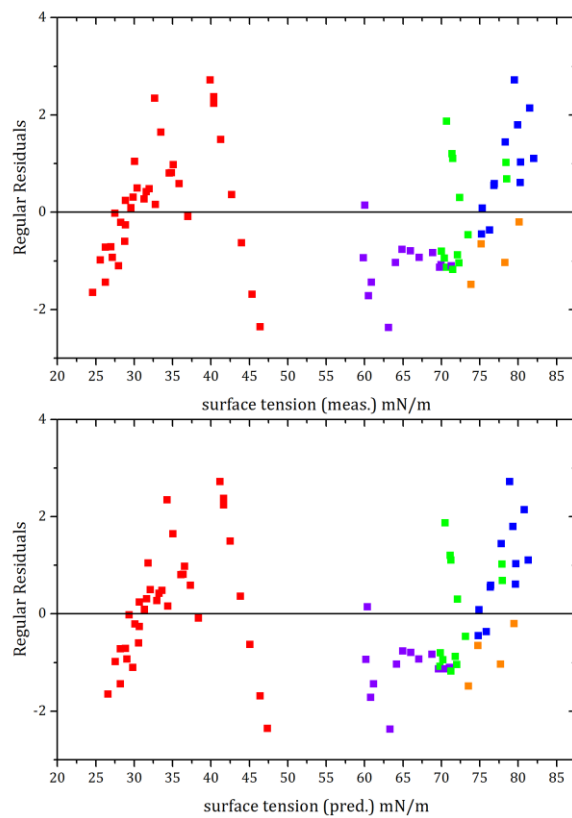
**Table S2:** Equation 6 evaluated for solutions containing one, two, and three solutes.

Number of solutes ( $n$ )	$C_i$
$n=1$	$C_A = \frac{r_A N_{AS}^2}{(N_A - N_{AS})(N_{WS} - r_A N_{AS})}$
$n=2$	$C_A = \frac{r_A N_{AS}^2}{N_A - N_{AS}} \left( \frac{\left( \frac{N_{WS} - r_A N_{AS}}{\chi_{AB}} \right)^{r_A/r_B}}{(N_{WS} - r_A N_{AS}) \chi_{AB}} \right)^{1/2}$
$n=3$	$C_A = \frac{r_A N_{AS}^2}{N_A - N_{AS}} \left( \frac{\left( \frac{(N_{WS} - r_A N_{AS}) \chi_{AC}^2}{\chi_{AB} \chi_{ABC}^2} \right)^{r_A/r_B} \left( \frac{(N_{WS} - r_A N_{AS}) \chi_{AB}^2}{\chi_{AC} \chi_{ABC}^2} \right)^{r_A/r_C}}{\chi_{AB} \chi_{AC} (N_{WS} - r_A N_{AS})^2 \chi_{ABC}^2} \right)^{1/6}$

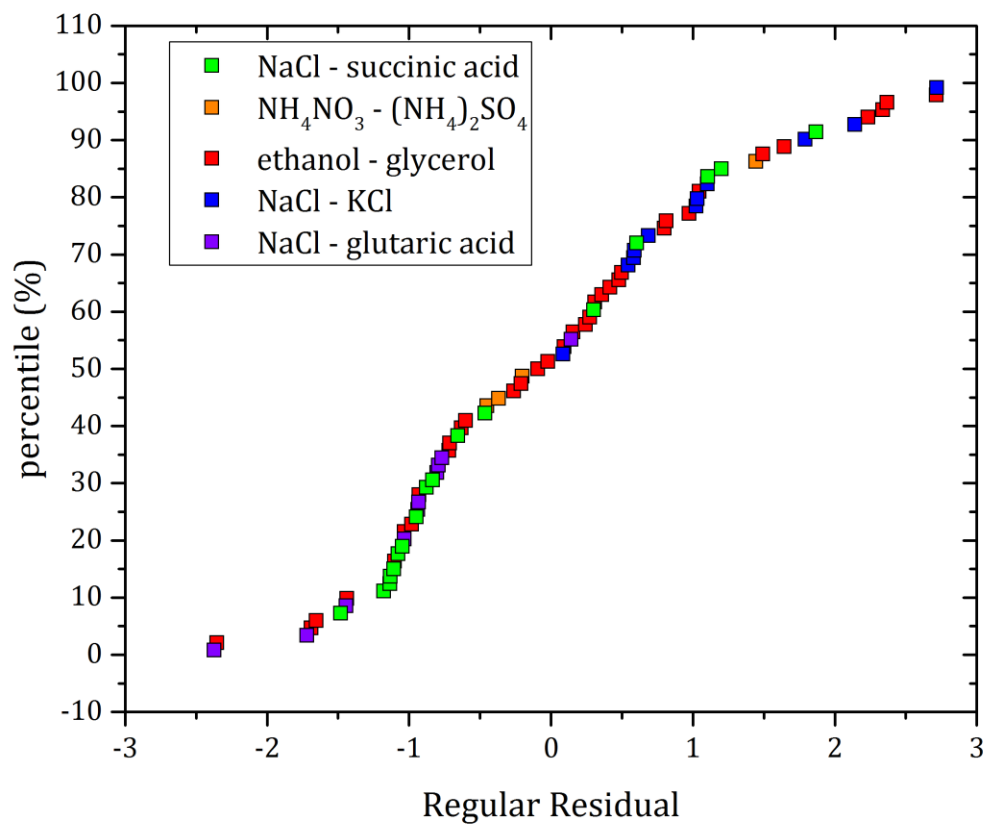


**Table S3:** Equation 7 evaluated for solutions containing one, two, and three solutes.

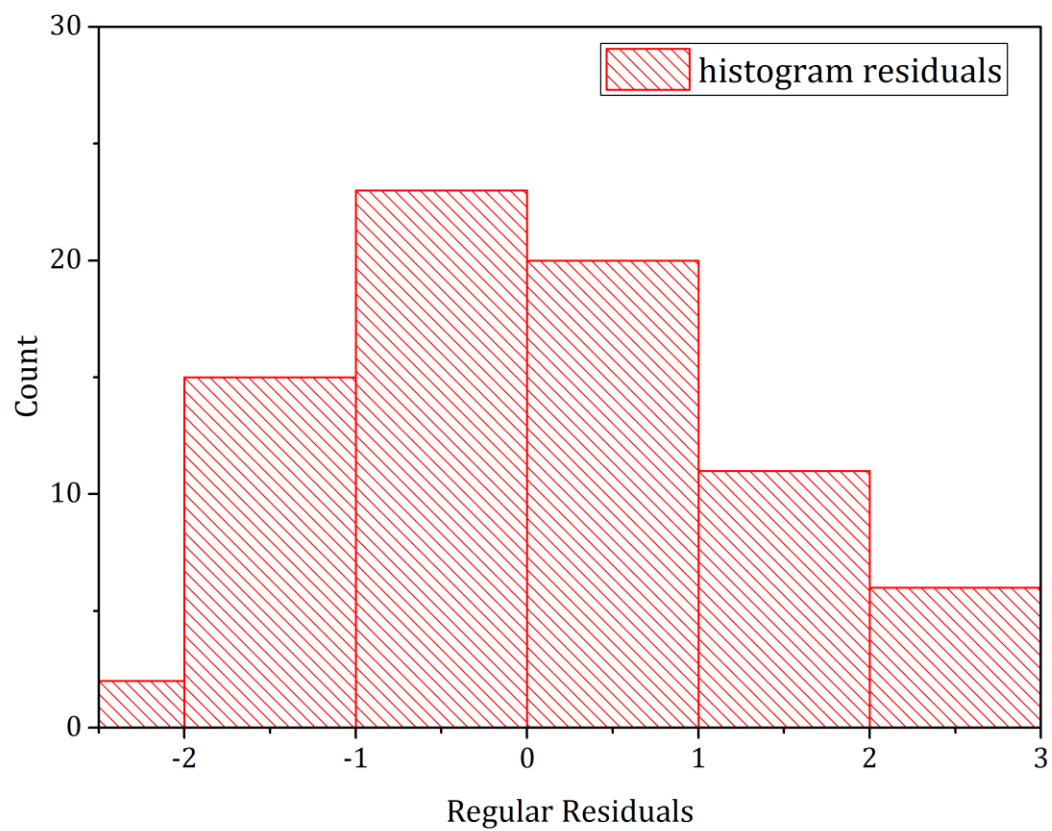
Number of solutes ( $n$ )	Surface Tension ( $\sigma$ )
$n=1$	$\sigma = \sigma_w + \frac{kT}{r_A S_w} \text{Ln} \left( \frac{N_{WS} - r_A N_{AS}}{N_{WS}} \right)$
$n=2$	$\sigma = \sigma_w + \frac{kT}{2r_A S_w} \text{Ln} \left[ \frac{\chi_{AB}(N_{WS} - r_A N_{AS})}{N_{WS}(N_{WS} - r_B N_{BS})} \right] + \frac{kT}{2r_B S_w} \text{Ln} \left[ \frac{\chi_{AB}(N_{WS} - r_B N_{BS})}{N_{WS}(N_{WS} - r_A N_{AS})} \right]$
$n=3$	$\begin{aligned} \sigma = \sigma_w + \frac{kT}{6r_A S_w} \text{Ln} \left[ \frac{\chi_{AB}\chi_{AC}\chi_{ABC}^2(N_{WS} - r_A N_{AS})^2}{N_{WS}^2 \chi_{BC}^2(N_{WS} - r_B N_{BS})(N_{WS} - r_C N_{CS})} \right] \\ + \frac{kT}{6r_B S_w} \text{Ln} \left[ \frac{\chi_{AB}\chi_{BC}\chi_{ABC}^2(N_{WS} - r_B N_{BS})^2}{N_{WS}^2 \chi_{AC}^2(N_{WS} - r_A N_{AS})(N_{WS} - r_C N_{CS})} \right] \\ + \frac{kT}{6r_C S_w} \text{Ln} \left[ \frac{\chi_{AC}\chi_{BC}\chi_{ABC}^2(N_{WS} - r_C N_{CS})^2}{N_{WS}^2 \chi_{AB}^2(N_{WS} - r_A N_{AS})(N_{WS} - r_B N_{BS})} \right] \end{aligned}$



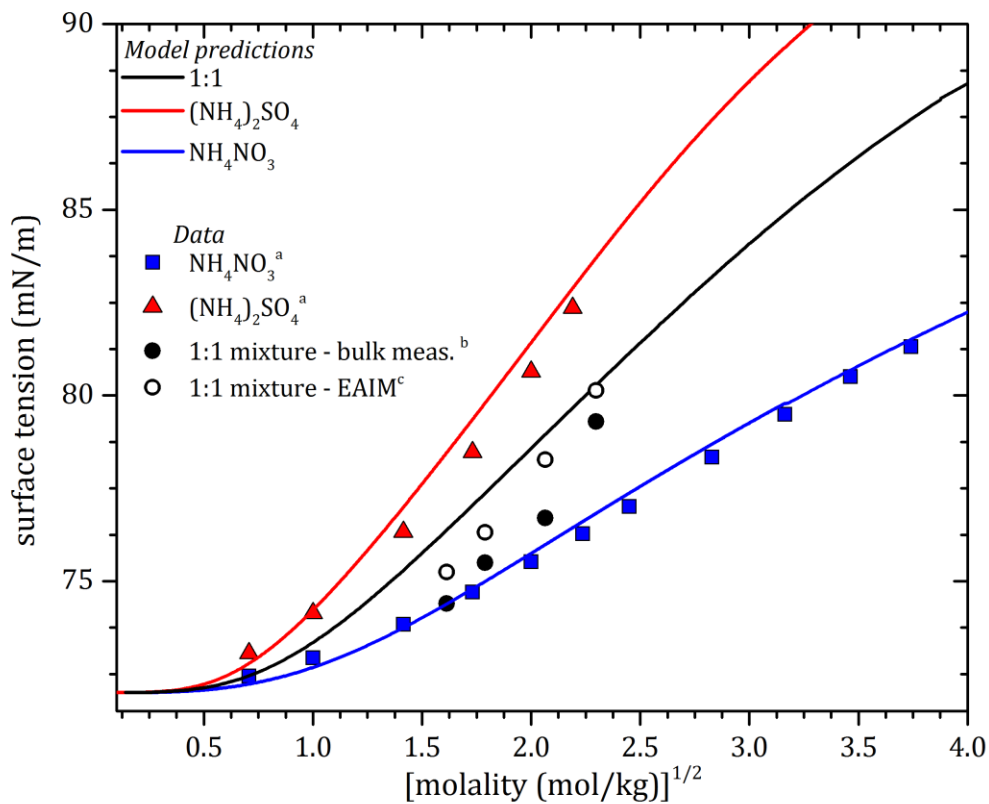
**Figure S1:** Residuals for surface tension ( $\sigma$ ) model predictions and measurements for various aqueous solutions: Ethanol-glycerol (red),<sup>1</sup> NaCl-KCl (blue)<sup>2</sup>, NaCl-succinic acid (green)<sup>3</sup>,  $\text{NH}_4\text{NO}_3 - (\text{NH}_4)_2\text{SO}_4$  (orange; taken by author with Wilhelmy plate), NaCl-glutaric acid (purple; optical tweezers).



**Figure S2:** Regular residuals and their percentiles for all systems studied.



**Figure S3:** Histogram plot of regular residuals for all systems studied in this work.



**Figure S4:** Surface tension model predictions and measurements vs. square root of molality for the ternary system consisting of  $\text{NH}_4\text{NO}_3$  (AN) and  $(\text{NH}_4)_2\text{SO}_4$  (AS) mixtures in aqueous solutions. The plot is similar to Figure 5 in the manuscript, except 3 model parameters are used to parametrize AS and 1 parameter for AN. Data sources: <sup>a</sup>ammonium nitrate and ammonium sulfate (Washburn et al,1928<sup>39</sup>), <sup>b</sup>1:1 mole ratio (measured with Digital Tensiometer K10ST by Krüss).